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Synthesis and Characterization

Polymerization of 4,4'-Difluorodiphenylether by Reaction with n-Butyllithium

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SUMMARY

Partial elucidation of the mechanism of polymerization of 4,4'-difluorodiphenylether by reaction with n-butyllithium to poly-oxy-biphenyl and poly-oxy-biphenylene is described. It could be afforded after considering the results of trapping experiments using carbon dioxide, water, deuterium oxide or furan. The intermediates of the first steps of the reaction are proposed. IR, NMR, and mass spectra of different derivatives suggest a complex reaction mechanism with the participation of different species, involving metalation reactions of 4,4'-difluorodiphenylether, elimination toward dehydroaromatic species with nucleophilic addition reactions and elimination of lithium fluoride leading to both biphenylic and biphenylenic structures. These polymers showed outstanding properties, particularly those common to aromatic polymers such as great thermal stability.

INTRODUCTION

Polymers with biphenylic structures in the backbone have been obtained from different ways, some of them involving dehydroaromatic or lithium-dehydroaromatic species (1,2) as intermediates in their generation. The polymers with perfluoro-substituted biphenylenic structures (3) showed high thermal and chemical stability.

The present paper is concerned with the synthesis of polymers from 4,4'-difluorodiphenylether using n-BuLi as metalating agent. A mechanism for the polymerization reaction is discussed in terms of the intermediates proposed in equation 1. Some of them, those with the lowest molecular weights, were trapped in different reactions as shown in equations 2,3 and 4.

EXPERIMENTAL

Apparatus and procedures. All melting points were uncorrected and determined on a Buchi-model Dr. Tottoli apparatus. ^{1}Hnmr and ^{19}Fnmr were recorded on a Varian T-60 instrument with tetramethylsilane as internal standard and carbon tetrachloride as solvent. Infrared spectra were recorded on an ir-8 or ir-12

Beckmann instrument. Mass spectra were registered on a MS-902 instrument or a combined Perkin-Elmer model 990 chromatograph with a Du-Pont 21-490 mass-spectrometer (GC-MS) at 70 ev. G.L.C. analyses were made on a Varian 2400 Gas-chromatograph having a column, packed with OV-101; 1,5% Chromosorb G 10, 120H/P. 4,4'-Difluorodiphenyl ether was purchased from Pierce Chemical Co(U.S.A.). Diethyl ether and THF were purified and dried by conventional methods and distilled prior to use. All organometallic reactions were carried out in an atmosphere of dry oxygen-free nitrogen. Solutions of n-butyllithium in diethyl ether were prepared by halogen-metal interconversion reactions between n-butylbromide and lithium metal using established procedures (4). The organometallic content was determined by Gilman double titration method(5).

General procedure of metalation of Difluorodiphenylether (DFDO)

A 100 ml, three necked, round-bottomed flask fitted with an adapter and a condenser to which a gas inlet tube was attached, was throughly dried with a flame. All organometallic reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. The solution of n-butyllithium in ether-THF was placed into the flask. Then, the cooled solution of DFDO was dropped into the flask over 15', stirred and maintained in conditions of temperatures and times as those specified in each reaction.

Metal-Hydrogen Interconversion from 4,4'-DFDO. Ratio 4,4'-DFDO to n-butyllithium 1:2.2.

A solution of 4,4'-DFDO (0.309 g, 0.0015 mol) in 5 ml of diethylether-THF (1:1) was added dropwise, to a stirred precooled (-80°C) solution of 0.0036 mol of n-butyllithium in 5 ml of diethylether-THF (1:1). The temperature was maintained below -80°C(3h).In a second run the temperature was maintained at -80°C(3h), -50°C(3h) and in a third experience -80°C(3h), -50°C(3h), -30°C(3h).

Reaction with carbon dioxide: The previous organometallic mixture was carbonated by bubbling carbon dioxide into the reaction. The mixture was then hydrolyzed with 10 ml of water and phase separated. The expected acids were precipitated from the water solution by the addition of concentrated HCl. The products were separated by preparative thin layer chromatography which led to 4,4'-difluorodiphenylether-3-carboxylic acid, m.p. 154-155°C(benzene). ^{19}Fnmr (diethylether-ethanol): (F)-4': 119; (F)-4: 115,7 ppm. IR(KBr pellet): 1679, 1620, 1575, 1550, 1450, 1300, 1285, 1220, 1195, 1140, 1120, 1080, 1065, 1005, 862, 845, 785, 690, 665, 595, 532, and 448 cm^{-1}, and 4,4'-difluorodiphenylether -2,3-dicarboxylic acid, m.p. 180°C(d). ^{19}Fnmr(diethylether-ethanol): (F)-4': 118; (F)-4: 113,7 ppm. IR(KBr pellet): 2200-3200, 1720, 1610, 1515, 1480, 1265, 1200, 940, 850, 840, 830 cm^{-1}.

Reaction with carbon dioxide-diazomethane: The mixture of acids obtained as previously specified was treated with diazomethane in diethylether and then chromatographed on silica gel Merck using benzene as eluent. Fnaction 1 afforded 4,4'-difluorodiphenylether-3-carboxymethyl ester, colorless liquid, M^{+}: 264. Retention time GC: 7'. ^{1}Hnmr: δ = 3,83 (3H,s), δ =6,87-7,58 (7H,m). Fraction II gave 4,4'-difluordiphenylether-2,3-dicarboxydimethyl ester, colorless liquid. M^{+}: 322. Retention time GC: 10'35". ^{1}Hnmr: δ=3,83 (3H,s), δ: 3.78 (3H,s), δ:6,86-7.18 (6H,m).

The metalation reaction carried out at -80°C (3h), -50°C(3h) led to a mixture of esters. Fractionation of the obtained mixtures was possible by GC-MS. The results obtained are in table A.

Reaction with deuterium oxide: To the previous organometallic mixtures 2 ml of deuterium oxide, 99.2% w/w was added. The organic phase was dried over magnesium sulfate. The residue that remained after evaporation of the organic solvent was analyzed by mass spectrometry at 20 ev (table B) and by ^{1}Hnmr spectroscopy. The reaction products showed a decrease in the signals due to aromatic protons as the reaction time and temperature increases.

Reaction with furan: To the previous organometallic mixtures, 0.070 mol of anhydrous freshly distilled furan was added and allow to reach room temperature and finally boiled for some minutes. The oily residue obtained after elimination of the solvent was extracted with a large amount of boiling light petroleum ether and chromatographed on silica gel (eluent: chloroform/ acetone 20:1). The fraction with Rf: 0.80 was identified as 6-(4'-flurofenoxide) -1,4-dihydronaphthalene-1,4-endoxide, m.p. 79-80°C (benzene), M^+ : 254. ^{1}Hnmr: δ: 6.8-7.18 (8H,m), δ: 6.6(1 H).

Polymerization: The previous organometallic mixture was allowed to warm up to room temperature gradually (-50°C/30 min., -30°C/30 min., -10°C/30 min., 0°C/ 30 min.) and finally boiled for an hour. The mixture was hydrolyzed by adding 10 ml of water and the organic layer removed by aspiration. The residue was extracted in a Soxhlet extractor with 20 ml fractions of petroleum ether, carbon tetrachloride, chloroform, acetone, ethanol, methanol and finally water. The yield after drying was 37.4% of a brown-yellow product which was infusible at temperatures up to 360°C.

Solubility of the polymer: The brown-yellow product, 0.020 g, previously obtained, was extracted in a Soxhlet extractor with the following solvents: n-propylalcohol, dimethylformamide, dimethylsulphoxide, acetonitrile, hydrochloric acid and diethyl ether. Elimination of the solvents left no observable residue. The insoluble fraction was washed with large amounts of water and dried. Elementhal analyses: calculated for: $C_{60}H_{30}O_5F_2Li_2$%: C, 80.89; H, 3.37. Found: C, 78.4; H, 3.78. Its Ir spectrum (KBr pellet) showed bands at: 2940, 1470, 940, 705 and 695 cm^{-1}.

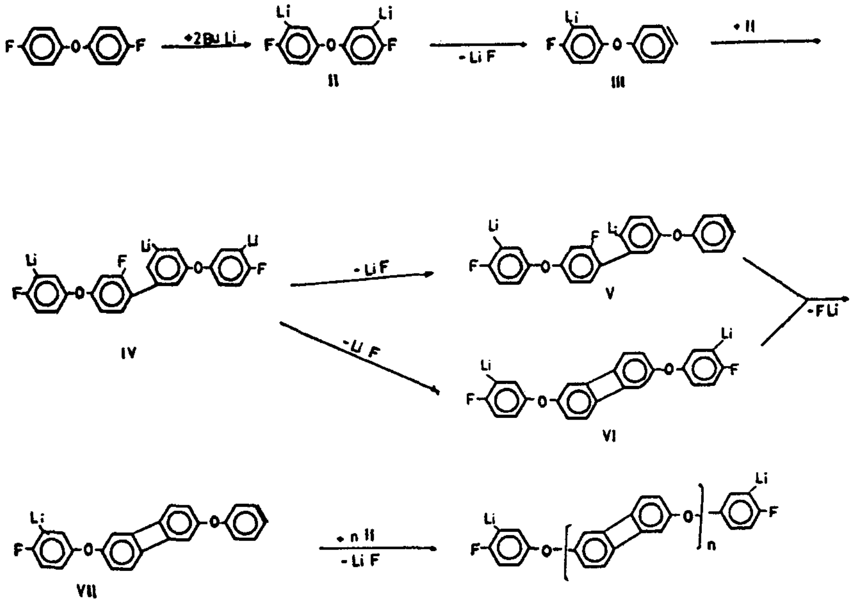
Isothermal aging of the polymer: The brown-yellow powder submitted to temperatures of 400°C in the presence of air showed the following loss of weight:

Time in hours	Weight loss, %
1	11
2	25.3
3	39.7
4	75.4

RESULTS AND DISCUSSION

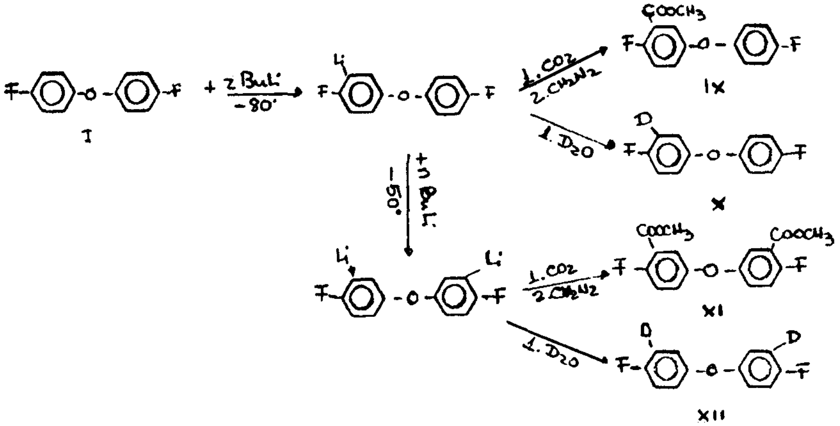
Polymerization of 4,4'-difluorodiphenylether I was carried out in tetrahydrofuran-diethyl ether using n-butyllithium as metalating agent . In order to elucidate the mechanism of reaction, different experiments were programmed changing times and temperatures with the object to know the progress of the polymerization, scheme 1.

1)



Thus, after 3 hours of reaction at -80°C the principal product was obtained through the monolithiation of 4,4'-difluorodiphenyl ether, then after 3 hours at -50°C the formation of dilithio and some trilithio-derivatives products was demonstrated such as we propose in scheme 2.

2)



The ortho-metalation of I was conveniently demonstrated by ^{1}H-NMR ^{19}F-NMR and mass spectra their derivatives.

Programmation of the reaction at longer times and temperatures (-30°C, three hours), led us to a mixture of different metalated products, such as evidenced with the results of GC/MS analysis of the mixture of reaction after trapping experiments with carbon dioxide-diazomethane. Tri- and tetrametalated

products derived from 4,4'-diflurodiphenylether could be also proposed according to these results.
Table A shows peaks and probable structures obtained from a GC-MS analysis of the product of metalation, after reaction with carbondioxide and diazomethane.

Table A: Results of GC/MS analysis of esters originated from reactions of the organometalated mixture with carbon dioxide and diazomethane.

peak	m/e	retention time	probable structure		method of analysis
1	264	5'	4,4'-DFDO-2-CO2CH3	$C_{14}H_{10}O_3F_3^{+\cdot}$	MS/nmr
2	264	7'	4,4'-DFDO-3-CO2CH3	$C_{14}H_{10}O_3F_2^{+\cdot}$	MS/nmr
3	244	8' 30"	N.I.		MS
4	322	9' 30"	4,4'-DFDO-2,2'-(CO2CH3)$_2$	$C_{16}H_{12}O_5F_2^{+\cdot}$	MS/nmr
5	322	10' 35"	4,4'-DFDO-2,5-(CO2CH3)$_2$	$C_{16}H_{12}O_5F_2^{+\cdot}$	MS/nmr
6	322	12' 5"	4,4'-DFDO-(CO2CH3)$_2$	$C_{16}H_{12}O_5F_2^{+\cdot}$	MS
7	322	13' 45"	4,4'-DFDO-(CO2CH3)$_2$	$C_{16}H_{12}O_5F_2$	MS
8	322	14' 12"	4,4'-DFDO-3,3'-(CO2CH3)$_2$	$C_{16}H_{12}O_5F_2^{+\cdot}$	MS/nmr
9	380	15' 15"	4,4'-DFDO-(CO2CH3)$_3$	$C_{18}H_{14}O_7F_2^{+\cdot}$	MS
10	360	16' 40"	4,4'-DFDO-(CO2CH3)$_2$ C_4H_9	$C_{20}H_{20}O_5F_2^{+\cdot}$	MS/nmr
11	380	18' 10"	4,4'-DFDO-(CO2CH3)$_3$	$C_{18}H_{14}O_7F_2^{+\cdot}$	MS
12	360	19' 15"	4,4'-DFDO-(CO2CH3)$_3C_4H_9$	$C_{20}H_{20}O_5F_2^{+\cdot}$	MS
13	438	21' 21"	4,4'-DFDO-(CO2CH3)$_4$	$C_{20}H_{16}O_9F_2^{+\cdot}$	MS
14	-	23' 30"	N.I.		

N.I. = no identification; DFDO = Difluorodiphenyl ether; MS = mass spectra

nmr = nuclear magnetic resonance

Product XI (peak 8) was also purified by column and preparative thin layer chromatography and could be identified spectroscopically. The product with m/e 360 also showed absorption bands at ir 3000 cm^{-1} showing aliphatic bonds. The ^{1}H-nmr spectra showed a ratio aliphatic to aromatic protons in agreement with the proposed structures for peaks 10 or 12.

The identification of some of the organolithium derivatives involved in the initial steps of the reaction was also possible by trapping experiments with deuterium oxide; results are shown in Table B.

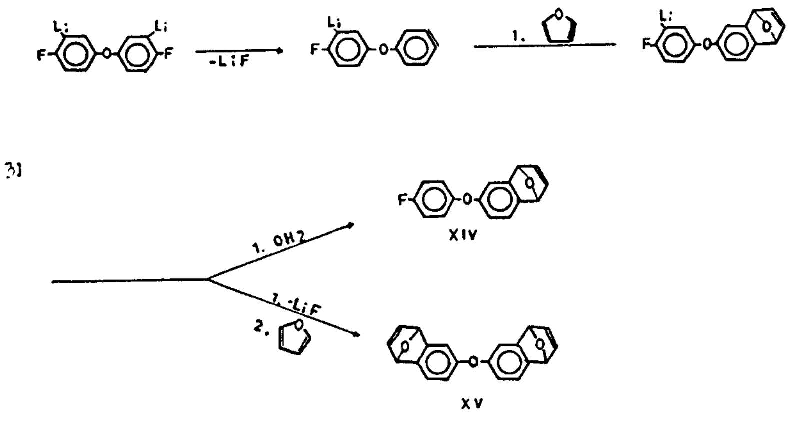
Differences in the relative intensities depending on the reaction conditions can be attributted to mono (m/e: 207; X), di-(m/e: 208; XII), tri-(m/e: 209) and tetradeuterated derivatives (m/e: 210), generated by successive replacement of lithium by deuterium atoms. The presence of a peak at m/e: 246 could also be attributed to butylderivatives probably originated by addition reactions.

TABLE B m/e values (relative intensities) from mass spectra analysis of products obtained by reactions of organometalated mixtures with deuterium oxide

relation m/e	4,4'-DFDO substrate	Metalation 3 hrs -80°	Metalation 3 hrs -80° 3 hrs -50°	Metalation 3 hrs -80° 3 hrs -50° 3 hrs -30°
206	100	100	23	22.5
207	13.4	52.7	100	30.5
208	1.0	7.9	26.6	26.3
209		0.3	2.3	4.0
210			1.0	1.0

DFDO = 4,4'-difluorodiphenyl ether

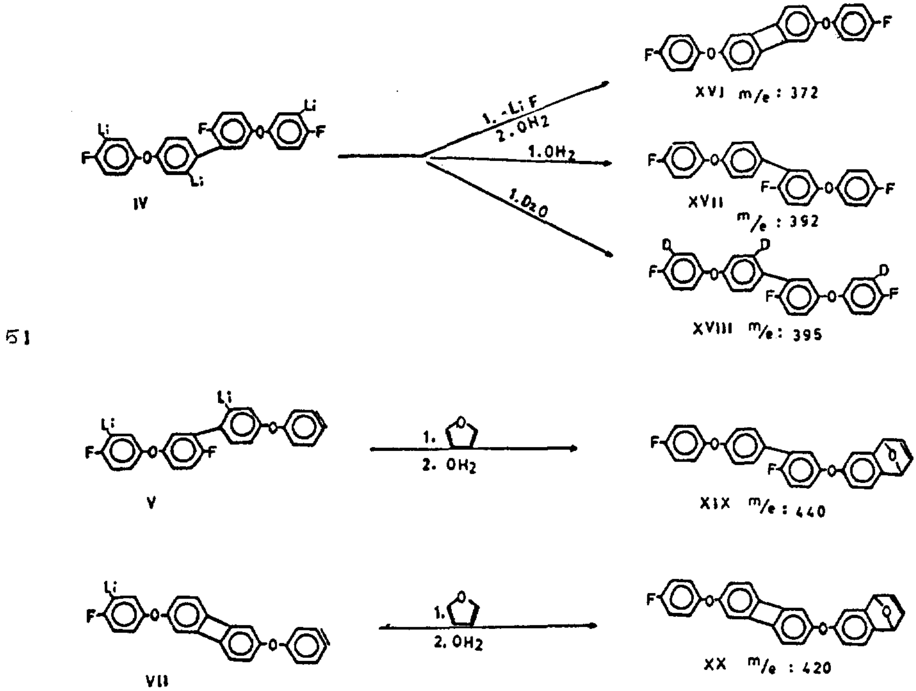
The presence of species such as III or VII could be evidenced by carrying out the reactions in the presence of furan. These species originated after lithium fluoride elimination involve dehydroaromatic species such as that proposed in scheme 3:



The structure of XIV: 6-(4'-fluorofenoxide) 1,4-dihydronaphthalene-1,4-endoxide was determined by ^{1}Hnmr spectroscopy. The allylic hydrogen showed peaks at δ : 6.6 in accordance with similar structures such as 1,4-epoxy-1,4-dihydronaphthalene. ^{19}Fnmr showed a singlet at 117.2 ppm. The mass spectrum gave a m/e: 254 and ir bands at 1265 (C-O-C) and 850-859 cm^{-1}. The presence of XV: 3,3'-6,6'-tetrahydro-3,6-3',6'-diepoxy-binaphthylether in the reaction mixture was detected in minimum quantities by mass-spectrometry at 20 ev, with m^{+} 302.

By prolonged heating of the reaction mixture at -30°C it was also possible to observe the presence of dimeric species such as IV, V and VII, according to mass spectra of the products obtained from quenching of the reaction mixture as shown in equation 4. The isolated products identified in this study as IX and XI indicate both mono- and dilithiation in the reaction of I with n-BuLi. The formation of XIV supports the participation of lithium dehydroaromatic derivatives in the proposed mechanism of polymerization (equation 1), while evidence for dimeric biphenylic structures such as IV has also been obtained from m/e: 395, XVIII; 392, XVIII and m/e: 372, XVI. (Scheme 4).

The results could indicate that the reaction of I with n-BuLi at low temperatures involves principally metalation of I to give II, elimination to dehydroaromatic species such as III, followed by nucleophilic addition reactions of the latter to II to give IV. This undergoes cyclization reaction with loss of lithium fluoride giving VI. Similar reactions of metalation, elimination, nucleophilic additions and cyclizations lead to the polymer.



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